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Chapter 14

Chemical Equilibrium

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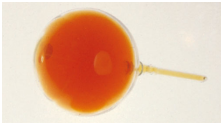
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Equilibrium

Equilibrium is a state in which there are no observable changes as time goes by.

Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant



Physical equilibrium

$$\text{H}_2\text{O} (l) \leftrightarrow \text{H}_2\text{O} (g)$$

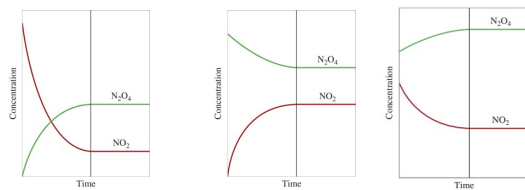
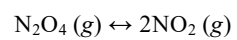
Chemical equilibrium

$$\text{N}_2\text{O}_4 (g) \leftrightarrow 2\text{NO}_2 (g)$$

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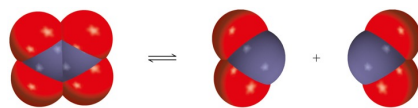
Equilibrium of N_2O_4 1



Start with NO_2

Start with N_2O_4

Start with NO_2 & N_2O_4



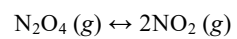
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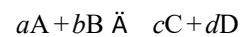
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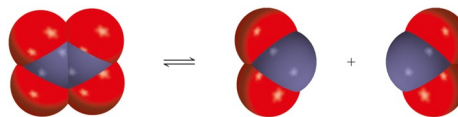
Equilibrium of N_2O_4 2



$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3}$$



$$K = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad \text{Law of Mass Action}$$



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Equilibrium of N_2O_4

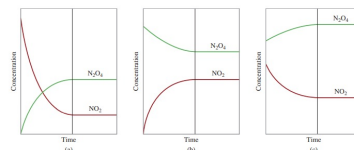


Table 14.1 The NO_2 - N_2O_4 System at 25°C .

Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium (Constant)	Ratio of Concentrations at Equilibrium (Constant)
$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$	$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

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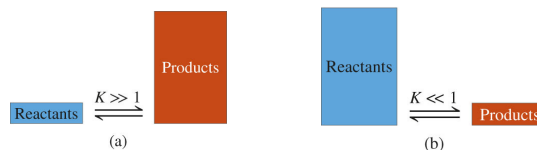
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Relationship of Equilibrium and K

$$K = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

Equilibrium Will

$K \gg 1$ Lie to the right Favor products
 $K \ll 1$ Lie to the left Favor reactants



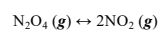
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Homogeneous Equilibrium 1

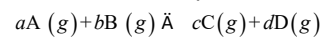
Homogeneous equilibrium applies to reactions in which all reacting species are in the same phase.



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \qquad K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

In most cases

$$K_c \neq K_p$$



$$K_p = K_c (RT)^{\Delta n}$$

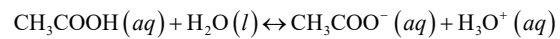
$$\Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants} = (c + d) - (a + b)$$

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Homogeneous Equilibrium 2



$$K'_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]} \qquad [\text{H}_2\text{O}] = \text{constant}$$

$$K'_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = K'_c[\text{H}_2\text{O}]$$

General practice **not** to include units for the equilibrium constant.

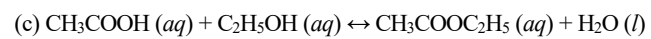
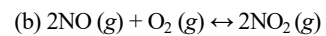
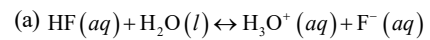
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Example 14.1 ₁

Write expressions for K_c , and K_p if applicable, for the following reversible reactions at equilibrium:



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Example 14.1 ₂

Strategy

Keep in mind the following facts: (1) the K_p expression applies only to gaseous reactions and (2) the concentration of solvent (usually water) does not appear in the equilibrium constant expression.

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Example 14.1 ₃

Solution

- (a) Because there are no gases present, K_p does not apply and we have only K_c .

$$K'_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}][\text{H}_2\text{O}]}$$

HF is a weak acid, so that the amount of water consumed in acid ionizations is negligible compared with the total amount of water present as solvent. Thus, we can rewrite the equilibrium constant as

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

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Example 14.1 ₄

$$(b) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} \quad K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}}$$

- (c) The equilibrium constant K'_c is given by

$$K'_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Because the water produced in the reaction is negligible compared with the water solvent, the concentration of water does not change. Thus, we can write the new equilibrium constant as

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

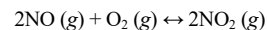
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Example 14.2 ₁

The following equilibrium process has been studied at 230°C:



In one experiment, the concentrations of the reacting species at equilibrium are found to be $[\text{NO}] = 0.0542 \text{ M}$, $[\text{O}_2] = 0.127 \text{ M}$, and $[\text{NO}_2] = 15.5 \text{ M}$. Calculate the equilibrium constant (K_c) of the reaction at this temperature.

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Example 14.2 ₂

Strategy

The concentrations given are equilibrium concentrations. They have units of mol/L, so we can calculate the equilibrium constant (K_c) using the law of mass action [Equation (14.2)].

Solution

The equilibrium constant is given by

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

Substituting the concentrations, we find that

$$K_c = \frac{(15.5)^2}{(0.0542)^2(0.127)} = 6.44 \times 10^8$$

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Example 14.2 ₃

Check

Note that K_c is given without units. Also, the large magnitude of K_c is consistent with the high product (NO_2) concentration relative to the concentrations of the reactants (NO and O_2).

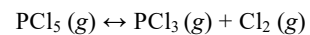
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Example 14.3 ₁

The equilibrium constant K_p for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine



is found to be 1.05 at 250°C. If the equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

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Example 14.3 ₂

Strategy

The concentrations of the reacting gases are given in atm, so we can express the equilibrium constant in K_p . From the known K_p value and the equilibrium pressures of PCl_3 and PCl_5 , we can solve for P_{Cl_2} .

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Example 14.3 ₃

Solution

First, we write K_p in terms of the partial pressures of the reacting species

$$K_p = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

Knowing the partial pressures, we write

$$1.05 = \frac{(0.463)(P_{\text{Cl}_2})}{(0.875)}$$

or

$$P_{\text{Cl}_2} = \frac{(1.05)(0.875)}{(0.463)} = \mathbf{1.98 \text{ atm}}$$

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Example 14.3 ₄

Check

Note that we have added atm as the unit for P_{Cl_2} .

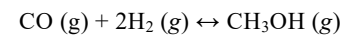
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Example 14.4 ₁

Methanol (CH_3OH) is manufactured industrially by the reaction



The equilibrium constant (K_c) for the reaction is 10.5 at 220°C. What is the value of K_p at this temperature.

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Example 14.4₂

Strategy

The relationship between K_c and K_p is given by Equation (14.5). What is the change in the number of moles of gases from reactants to product? Recall that

Δn = moles of gaseous products – moles of gaseous reactants

What unit of temperature should we use?

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Example 14.4₃

Solution

The relationship between K_c and K_p is

$$K_p = K_c (0.0821 T)^{\Delta n}$$

Because $T = 273 + 220 = 493$ K and $\Delta n = 1 - 3 = -2$, we have

$$\begin{aligned} K_p &= (10.5)(0.0821 \times 493)^{-2} \\ &= 6.41 \times 10^{-3} \end{aligned}$$

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Example 14.4 ₄

Check

Note that K_p like K_c , is a dimensionless quantity. This example shows that we can get a quite different value for the equilibrium constant for the same reaction, depending on whether we express the concentrations in moles per liter or in atmospheres.

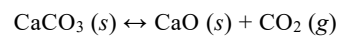
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Heterogeneous Equilibrium ₁

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases**.



$$K'_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \quad \begin{array}{l} [\text{CaCO}_3] = \text{constant} \\ [\text{CaO}] = \text{constant} \end{array}$$

$$K_c = [\text{CO}_2] = K'_c \times \frac{[\text{CaCO}_3]}{[\text{CaO}]} \quad K_p = P_{\text{CO}_2}$$

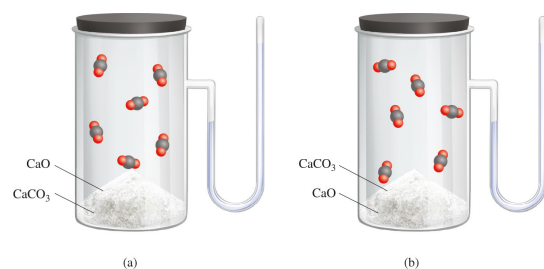
The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

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Heterogeneous Equilibrium 2



P_{CO_2} does not depend on the amount of CaCO_3 or CaO

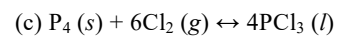
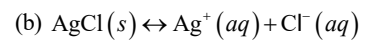
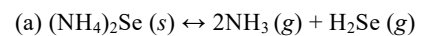
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Example 14.5 1

Write the equilibrium constant expression K_c , and K_p if applicable, for each of the following heterogeneous systems:



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Example 14.5₂

Strategy

We omit any pure solids or pure liquids in the equilibrium constant expression because their activities are unity.

Solution

- a) Because $(\text{NH}_4)_2\text{Se}$ is a solid, the equilibrium constant K_c is given by

$$K_c = [\text{NH}_3]^2 [\text{H}_2\text{Se}]$$

Alternatively, we can express the equilibrium constant K_p in terms of the partial pressures of NH_3 and H_2Se :

$$K_p = P_{\text{NH}_3}^2 P_{\text{H}_2\text{Se}}$$

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Example 14.5₃

- b) Here AgCl is a solid so the equilibrium constant is given by

$$K_c = [\text{Ag}^+][\text{Cl}^-]$$

Because no gases are present, there is no K_p expression.

- c) We note that P_4 is a solid and PCl_3 is a liquid, so they do not appear in the equilibrium constant expression. Thus, K_c is given by

$$K_c = \frac{1}{[\text{Cl}_2]^6}$$

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Example 14.5 ₄

Alternatively, we can express the equilibrium constant in terms of the pressure of Cl₂:

$$K_p = \frac{1}{P_{\text{Cl}_2}^6}$$

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Example 14.6 ₁

Consider the following heterogeneous equilibrium:



At 800°C, the pressure of CO₂ is 0.236 atm. Calculate (a) K_p and (b) K_c for the reaction at this temperature.

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Example 14.6₂

Strategy

Remember that pure solids do not appear in the equilibrium constant expression. The relationship between K_p and K_c is given by Equation (14.5).

Solution

a) Using Equation (14.8) we write

$$\begin{aligned} K_p &= P_{\text{CO}_2} \\ &= \mathbf{0.236} \end{aligned}$$

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Example 14.6₃

(b) From Equation (14.5), we know

$$K_p = K_c (0.0821 T)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073\text{K}$ and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$0.236 = K_c (0.0821 \times 1073)$$

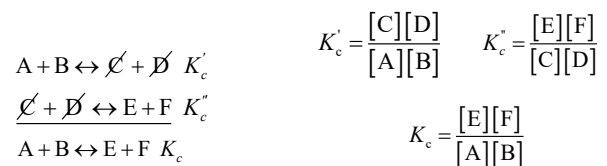
$$K_c = \mathbf{2.68 \times 10^{-3}}$$

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Equilibrium Constants 1



$$K_c = K_c' \times K_c''$$

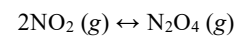
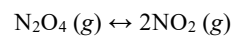
If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

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Equilibrium Constants 2



$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

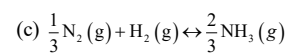
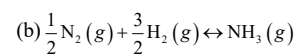
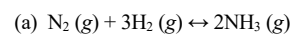
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Example 14.7 ₁

The reaction for the production of ammonia can be written in a number of ways:



Write the equilibrium constant expression for each formulation.
(Express the concentrations of the reacting species in mol/L.)

d) How are the equilibrium constants related to one another?

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Example 14.7 ₂

Strategy

We are given three different expressions for the same reacting system. Remember that the equilibrium constant expression depends on how the equation is balanced, that is, on the stoichiometric coefficients used in the equation.

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Example 14.7 ₃

Solution

$$(a) \quad K_a = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$(b) \quad K_b = \frac{[\text{NH}_3]}{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}}}$$

$$(c) \quad K_c = \frac{[\text{NH}_3]^{\frac{2}{3}}}{[\text{N}_2]^{\frac{1}{3}}[\text{H}_2]}$$

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Example 14.7 ₄

$$(d) \quad K_a = K_b^2$$

$$K_a = K_c^3$$

$$K_b^2 = K_c^3 \text{ or } K_b = K_c^{\frac{3}{2}}$$

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Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in M . In the gaseous phase, the concentrations can be expressed in M or in atm.
2. The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
5. If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

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Chemical Kinetics and Chemical Equilibrium



Equilibrium
 $\text{rate}_f = \text{rate}_r$

$$k_f [A][B]^2 = k_r [AB_2]$$

$$\frac{k_f}{k_r} = K_c = \frac{[AB_2]}{[A][B]^2}$$

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Reaction Quotient

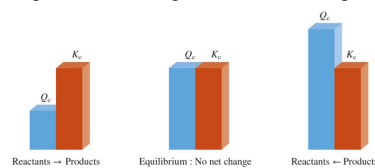
The **reaction quotient** (Q_c) is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.

IF

$Q_c < K_c$ system proceeds from left to right to reach equilibrium

$Q_c = K_c$ the system is at equilibrium

$Q_c > K_c$ system proceeds from right to left to reach equilibrium



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Example 14.8 ₁

Strategy

We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations and hence the reaction quotient (Q_c). How does a comparison of Q_c with K_c enable us to determine if the system is at equilibrium or, if not, in which direction will the net reaction proceed to reach equilibrium?

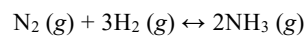
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Example 14.8 ₂

At the start of a reaction, there are 0.249 mol N₂, 3.21×10⁻² mol H₂, and 6.42×10⁻⁴ mol NH₃ in a 3.50-L reaction vessel at 375°C. If the equilibrium constant (K_c) for the reaction



is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

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Example 14.8 ₃

Solution

The initial concentrations of the reacting species are

$$K_p = P_{\text{CO}_2}$$

$$[\text{H}_2]_0 = \frac{3.21 \times 10^{-2} \text{ mol}}{3.50 \text{ L}} = 9.17 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3]_0 = \frac{6.42 \times 10^{-4} \text{ mol}}{3.50 \text{ L}} = 1.83 \times 10^{-4} \text{ M}$$

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Example 14.8 4

Next we write

$$Q_c = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0 [\text{H}_2]_0^3} = \frac{(1.83 \times 10^{-4})^2}{(0.0711)(9.17 \times 10^{-3})^3} = 0.611$$

Because Q_c is smaller than K_c (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of NH_3 and a decrease in the concentrations of N_2 and H_2 . That is, the net reaction will proceed from left to right until equilibrium is reached.

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Calculating Equilibrium Concentrations

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown x , which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x .
3. Having solved for x , calculate the equilibrium concentrations of all species.

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Example 14.9 ₁

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C . The equilibrium constant K_c for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}(\text{g})$ is 54.3 at this temperature. Calculate the concentrations of H_2 , I_2 , and HI at equilibrium.

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Example 14.9 ₂

Strategy

We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no HI was present, the system could not be at equilibrium. Therefore, some H_2 would react with the same amount of I_2 (why?) to form HI until equilibrium was established.

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Example 14.9₃

Solution

We follow the preceding procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction is 1 mol H₂ reacting with 1 mol I₂ to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H₂ and I₂ at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

	H ₂	+	I ₂	↔	2HI
Initial (M):	0.500		0.500		0.000
Change (M):	$-x$		$-x$		$+2x$
Equilibrium (M):	$(0.500 - x)$		$(0.500 - x)$		$2x$

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Example 14.9₄

Step 2: The equilibrium constant is given by

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$

$$x = 0.393 \text{ M}$$

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Example 14.9_s

Step 3: At equilibrium, the concentrations are

$$[\text{H}_2] = (0.500 - 0.393) \text{ M} = \mathbf{0.107 \text{ M}}$$

$$[\text{I}_2] = (0.500 - 0.393) \text{ M} = \mathbf{0.107 \text{ M}}$$

$$[\text{HI}] = 2 \times 0.393 \text{ M} = \mathbf{0.786 \text{ M}}$$

Check You can check your answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

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Example 14.10_i

For the same reaction and temperature as in Example 14.9,
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}(\text{g})$,
 suppose that the initial concentrations of H_2 , I_2 , and HI are
 0.00623 M, 0.00414 M, and 0.0224 M respectively. Calculate
 the concentrations of these species at equilibrium.

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Example 14.10₂

Strategy

From the initial concentrations we can calculate the reaction quotient (Q_c) to see if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. A comparison of Q_c with K_c also enables us to determine if there will be a depletion in H_2 and I_2 or HI as equilibrium is established.

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Example 14.10₃

Solution

First we calculate Q_c as follows:

$$Q_c = \frac{[HI]_0^2}{[H_2]_0 [I_2]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

Because Q_c (19.5) is smaller than K_c (54.3), we conclude that the net reaction will proceed from left to right until equilibrium is reached (see Figure 14.4); that is, there will be a depletion of H_2 and I_2 and a gain in HI.

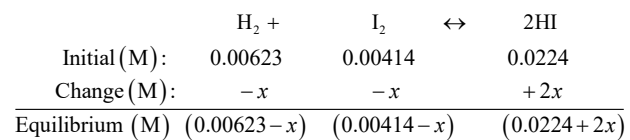
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Example 14.10₄

Step 1: Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be $2x$. Next we write



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Example 14.10₅

Step 2: The equilibrium constant is

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Substituting, we get

$$54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

It is not possible to solve this equation by the square root shortcut, as the starting concentrations $[\text{H}_2]$ and $[\text{I}_2]$ are unequal. Instead, we must first carry out the multiplications

$$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$$

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Example 14.10₆

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation (see Appendix 4) is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here we have $a = 50.3$, $b = -0.654$, and $c = 8.98 \times 10^{-4}$, so that

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$$x = 0.0114 M \quad \text{or} \quad x = 0.00156 M$$

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Example 14.10₇

The first solution is physically impossible because the amounts of H_2 and I_2 reacted would be more than those originally present.

The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for x is easy.

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.00623 - 0.00156) M = \mathbf{0.00467 M}$$

$$[I_2] = (0.00414 - 0.00156) M = \mathbf{0.00258 M}$$

$$[HI] = (0.0224 + 2 \times 0.00156) M = \mathbf{0.0255 M}$$

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Example 14.10 _s

Check

You can check the answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

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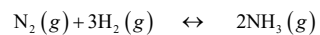
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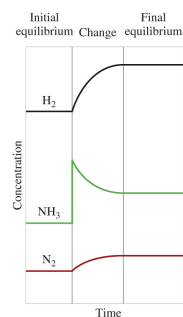
Le Châtelier's Principle ₁

If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

Changes in Concentration



Equilibrium shifts left ← Add NH_3
to offset stress



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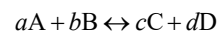
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Le Châtelier's Principle ₂

Changes in Concentration



<u>Change</u>	<u>Shifts the Equilibrium</u>
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

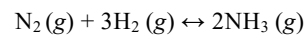
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Example 14.11 ₁

At 720°C, the equilibrium constant K_c for the reaction



is 2.37×10^{-3} . In a certain experiment, the equilibrium concentrations are $[\text{N}_2] = 0.683 \text{ M}$, $[\text{H}_2] = 8.80 \text{ M}$, and $[\text{NH}_3] = 1.05 \text{ M}$. Suppose some NH_3 is added to the mixture so that its concentration is increased to 3.65 M . (a) Use Le Châtelier's principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient Q_c and comparing its value with K_c .

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Example 14.11 ₂

Strategy

- (a) What is the stress applied to the system? How does the system adjust to offset the stress?
- (b) At the instant when some NH_3 is added, the system is no longer at equilibrium. How do we calculate the Q_c for the reaction at this point? How does a comparison of Q_c with K_c tell us the direction of the net reaction to reach equilibrium.

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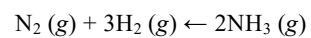
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Example 14.11 ₃

Solution

- (a) The stress applied to the system is the addition of NH_3 . To offset this stress, some NH_3 reacts to produce N_2 and H_2 until a new equilibrium is established. The net reaction therefore shifts from right to left; that is,



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Example 14.11 ₄

(b) At the instant when some of the NH_3 is added, the system is no longer at equilibrium. The reaction quotient is given by

$$\begin{aligned} Q_c &= \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0 [\text{H}_2]_0^3} \\ &= \frac{(3.65)^2}{(0.683)(8.80)^3} \\ &= 2.86 \times 10^{-2} \end{aligned}$$

Because this value is greater than 2.37×10^{-3} , the net reaction shifts from right to left until Q_c equals K_c .

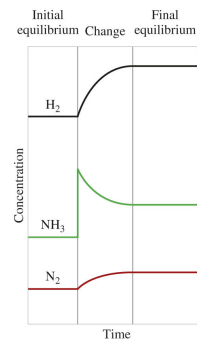
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Example 14.11 ₅

Figure 14.8 shows qualitatively the changes in concentrations of the reacting species.



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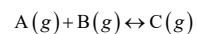
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Le Châtelier's Principle ₃

Changes in Volume and Pressure



<u>Change</u>	<u>Shifts the Equilibrium</u>
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

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Example 14.12 ₁

Consider the following equilibrium systems:

- (a) $2\text{PbS}(s) + 3\text{O}_2(g) \leftrightarrow 2\text{PbO}(s) + 2\text{SO}_2(g)$
- (b) $\text{PCl}_5(g) \leftrightarrow \text{PCl}_3(g) + \text{Cl}_2(g)$
- (c) $\text{H}_2(g) + \text{CO}_2(g) \leftrightarrow \text{H}_2\text{O}(g) + \text{CO}(g)$

Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature.

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Example 14.12₂

Strategy

A change in pressure can affect only the volume of a gas, but not that of a solid because solids (and liquids) are much less compressible. The stress applied is an increase in pressure.

According to Le Châtelier's principle, the system will adjust to partially offset this stress. In other words, the system will adjust to decrease the pressure. This can be achieved by shifting to the side of the equation that has fewer moles of gas. Recall that pressure is directly proportional to moles of gas:

$$PV = nRT \text{ so } P \propto n.$$

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Example 14.12₃

Solution

- a) Consider only the gaseous molecules. In the balanced equation, there are 3 moles of gaseous reactants and 2 moles of gaseous products. Therefore, the net reaction will shift toward the products (to the right) when the pressure is increased.
- b) The number of moles of products is 2 and that of reactants is 1; therefore, the net reaction will shift to the left, toward the reactant.
- c) The number of moles of products is equal to the number of moles of reactants, so a change in pressure has no effect on the equilibrium.

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Example 14.12 ₄

Check

In each case, the prediction is consistent with Le Châtelier's principle.

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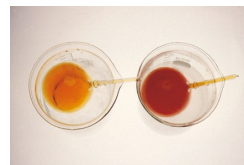
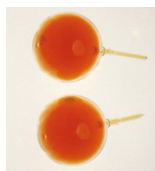
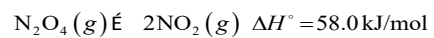
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Le Châtelier's Principle ₄

Changes in Temperature

<u>Change</u>	<u>Exothermic Rxn</u>	<u>Endothermic Rxn</u>
Increase temperature	K decreases	K increases
Decrease temperature	K increases	K decreases



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Le Châtelier's Principle ⁵

Adding a Catalyst

- does not change K
- does not shift the position of an equilibrium system
- system will reach equilibrium sooner



Catalyst lowers E_a for **both** forward and reverse reactions.
Catalyst does not change equilibrium constant or shift equilibrium.

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Le Châtelier's Principle - Summary

<u>Change</u>	<u>Shift Equilibrium</u>	<u>Change Equilibrium Constant</u>
Concentration	yes	no
Pressure	yes*	no
Volume	yes*	no
Temperature	yes	yes
Catalyst	no	no

*Dependent on relative moles of gaseous reactants and products

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Example 14.13 ₁

Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):



Predict the changes in the equilibrium if

- the reacting mixture is heated at constant volume;
- some N_2F_4 gas is removed from the reacting mixture at constant temperature and volume;
- the pressure on the reacting mixture is decreased at constant temperature; and
- a catalyst is added to the reacting mixture.

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Example 14.13 ₂

Strategy

- What does the sign of ΔH° indicate about the heat change (endothermic or exothermic) for the forward reaction?
- Would the removal of some N_2F_4 increase or decrease the Q_c of the reaction?
- How would the decrease in pressure change the volume of the system?
- What is the function of a catalyst? How does it affect a reacting system not at equilibrium? at equilibrium?

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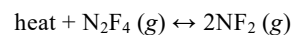
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Example 14.13 ₃

Solution

- a) The stress applied is the heat added to the system. Note that the $\text{N}_2\text{F}_4 \rightarrow 2\text{NF}_2$ reaction is an endothermic process ($\Delta H^\circ > 0$), which absorbs heat from the surroundings. Therefore, we can think of heat as a reactant



The system will adjust to remove some of the added heat by undergoing a decomposition reaction (from left to right).

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Example 14.13 ₄

The equilibrium constant

$$K_c = \frac{[\text{NF}_2]^2}{[\text{N}_2\text{F}_4]}$$

will therefore increase with increasing temperature because the concentration of NF_2 has increased and that of N_2F_4 has decreased. Recall that the equilibrium constant is a constant only at a particular temperature. If the temperature is changed, then the equilibrium constant will also change.

- b) The stress here is the removal of N_2F_4 gas. The system will shift to replace some of the N_2F_4 removed. Therefore, the system shifts from right to left until equilibrium is reestablished. As a result, some NF_2 combines to form N_2F_4 .

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Example 14.13 ₅

Comment

The equilibrium constant remains unchanged in this case because temperature is held constant. It might seem that K_c should change because NF_2 combines to produce N_2F_4 . Remember, however, that initially some N_2F_4 was removed. The system adjusts to replace only some of the N_2F_4 that was removed, so that overall the amount of N_2F_4 has decreased. In fact, by the time the equilibrium is reestablished, the amounts of both NF_2 and N_2F_4 have decreased. Looking at the equilibrium constant expression, we see that dividing a smaller numerator by a smaller denominator gives the same value of K_c .

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Example 14.13 ₆

- c) The stress applied is a decrease in pressure (which is accompanied by an increase in gas volume). The system will adjust to remove the stress by increasing the pressure. Recall that pressure is directly proportional to the number of moles of a gas. In the balanced equation we see that the formation of NF_2 from N_2F_4 will increase the total number of moles of gases and hence the pressure. Therefore, the system will shift from left to right to reestablish equilibrium. The equilibrium constant will remain unchanged because temperature is held constant.

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Example 14.13 ₇

- d) The function of a catalyst is to increase the rate of a reaction. If a catalyst is added to a reacting system not at equilibrium, the system will reach equilibrium faster than if left undisturbed. If a system is already at equilibrium, as in this case, the addition of a catalyst will not affect either the concentrations of NF_2 and N_2F_4 or the equilibrium constant.

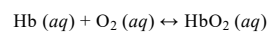
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Chemistry In Action

Life at High Altitudes and Hemoglobin Production



$$K_c = \frac{[\text{HbO}_2]}{[\text{Hb}][\text{O}_2]}$$



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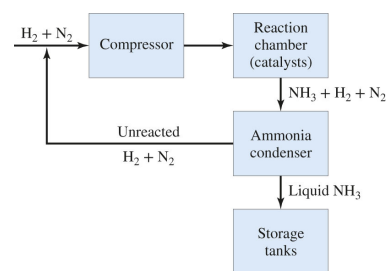
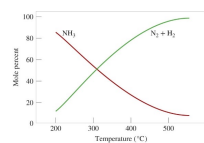
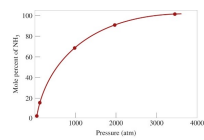
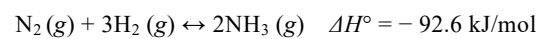
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Chemistry In Action: The Haber Process



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